

“COSY”谱用于昆明山海棠生物碱的鉴定

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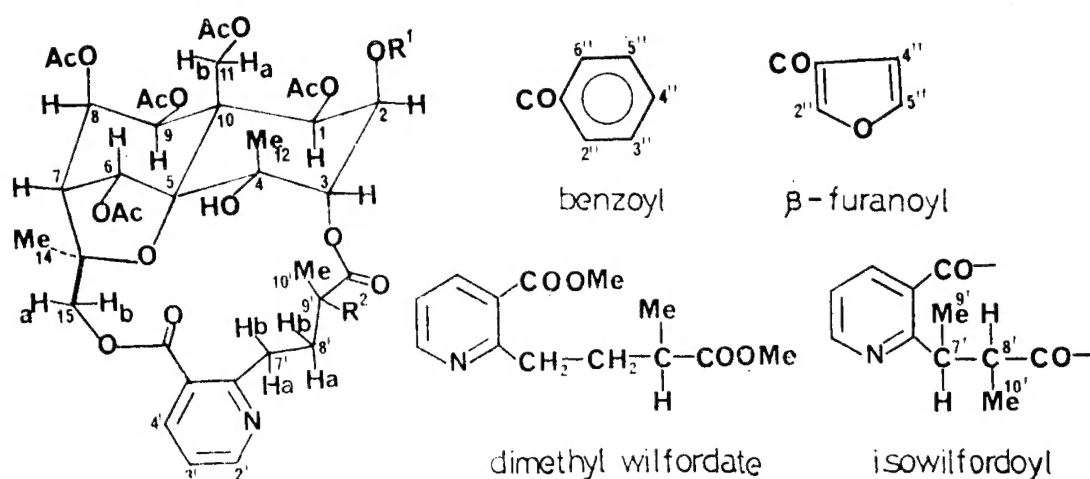
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摘要 昆明山海棠 (*Tripterygium hypoglaucum*) 的生物碱可从甲醇中结晶析出, 是多元混合物。高压液相色谱分析出现 5 个峰, 用制备性烷化硅胶 RP-18 薄层层析板分离纯化, 5 个生物碱逐一分开。用化学和光谱法证明为: 雷公藤次碱、雷公藤碱乙、雷公藤碱丁、雷公藤碱及卫矛碱 (1—5)。高压液相色谱分析指出, 前二者为其中的主要成分。用高分辨核磁共振谱及 COSY 谱指定了它们的质子及其在分子中的取向, 说明了它们之间结构和构型的关系。

关键词 昆明山海棠; 雷公藤次碱; 雷公藤碱乙; 雷公藤碱丁; 雷公藤碱; 卫矛碱; “COSY”谱

前报报道了从昆明山海棠 (*Tripterygium hypoglaucum* (Lévl) Hutch,) 分离和鉴定了雷公藤次碱 (wilforine) (1) [1]。昆明山海棠生物碱是多成分的混合物, 可从甲醇中结晶析出。硅胶柱高压液相色谱分析, 未能使其组分彼此分开 (图 1)。烷化硅胶 RP-18 柱高压液相色谱分析显示 5 个峰, 其主要成分为二, 即雷公藤次碱 (1) 和雷公藤碱乙 (wilforgine) (2) (图 2)。继用 RP-18 薄层层析板分离得五个生物碱成分, 除上述二者外, 为雷公藤碱 (wilfordine) (4) [7], 雷公藤碱丁 (wilfortrine) (3) 和卫矛碱 (euonymine) (5)。生物碱 (1—4) 最早从同属植物雷公藤 (*T. wilfordii* Hook. f.) 分离得 [5, 6], 后又从该植物分离和鉴定了雷公藤碱戊、雷公藤次碱及雷公藤碱 [2]。昆明山海棠的生物碱成分, 除雷公藤次碱 [1] 外, 尚未报道有关的研究。

昆明山海棠生物碱 (1—5) 的红外、紫外光谱差异不大, 质谱分析分别测得其分子量 (表 1)。它们的高分辨核磁共振谱使各质子信号清楚的分布于所测光谱范围内, 谱峰的归属则借助 “COSY” 谱 [3, 4] 提供的各有关质子群之间的自旋标量偶合关系。从生物碱 (1—5) 的 “COSY” 谱 (图 3—6, 生物碱 (3) 的 “COSY” 谱从略) 中的自旋偶合相关峰可辨认出 $H_1-H_2-H_3$, $H_7-H_8-H_9$ 之间的 3J 偶合关系, 而且偶合常数提示, 这些质子之间不存在 $a-a$ 键偶合, 也可辨认出 $H_{a11}-H_{b11}$ 之间的 2J 偶合, $Me_{14}-H_{b15}-H_{a15}$ 之间的 4J 和 2J 偶合, 以及 OH_4-Me_{12} 之间的 4J 偶合。从分子模型看, 由于五元环的并合, H_6 、 H_7 之间的双面夹角接近 90° , H_6 在五个生物碱中均呈单峰, 但在 “COSY” 谱中均出现 $Me_{14}-H_6-H_7$ 之间的自旋偶合相关峰, H_6-Me_{14} 已属 5J 远程偶合, 仍可观察到。



	R_1	R_2	大环酰基	倍半萜基醇
1. wilforine	benzoyl	H	wilfordoyl	euonyminol
2. wilforgine	β -furanoyl	H	"	"
3. wilfortrine	"	OH	9'-OH-wilfordoyl	"
4. wilfordine	benzoyl	OH	"	"
5. cuonymine	Ac		isowilfordoyl	"
6. dimethyl wilfordate				

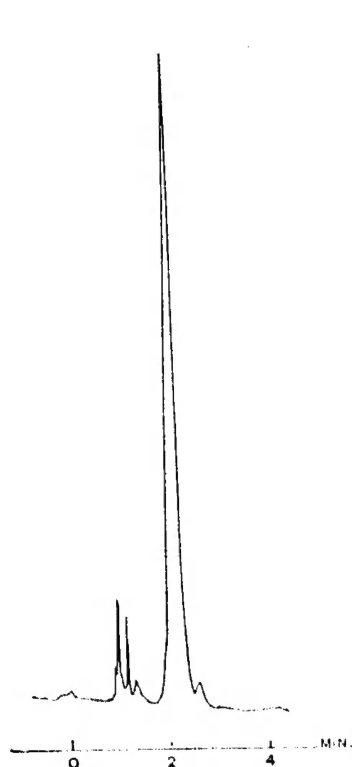


图1. 昆明山海棠生物碱的高压液相色谱
Fig1. 1. HPLC analytic chromatogram of the mixture alkaloids from *T. hypoglauca*.
column RP-18 (4.5 250mm),
 CHCl_3 -MeOH (9:1),
flow rate: 4ml/min,
detected at UV 254nm.

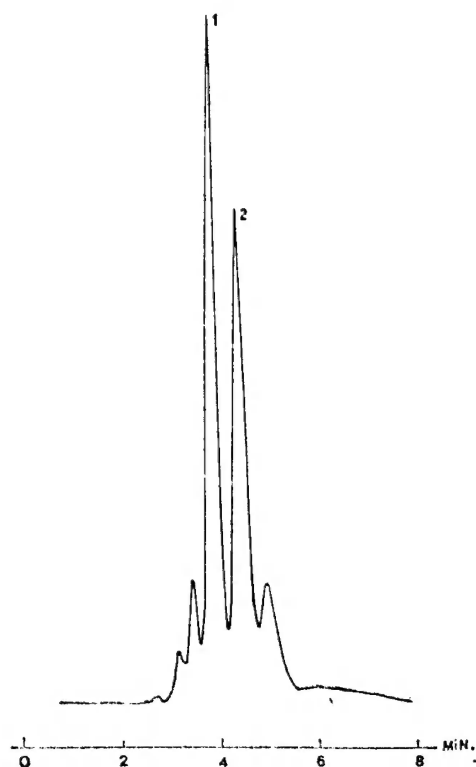


图2. 昆明山海棠生物碱的高压液相色谱
Fig. 2. HPLC analytic chromatogram of the mixture alkaloids from *T. hypoglauca*.
column RP-18(4.6 250mm),
MeOH- H_2O (88:12),
flow rate: 4ml/min,
detected at UV 254nm.
1. wilforgine; 2. wilforine.

雷公藤酰基、9'-OH-雷公藤酰基以及异雷公藤酰基与倍半萜基醇 euonyminol 构成了大环, 从它们的 “COSY” 谱可辨认出 $H_{7/a}-H_{7/b}-H_{8/a}-H_{8/b}-H_9-H_{10}$ (生物碱 1, 2), $H_{7/a}-H_{7/b}-H_{8/a}-H_{8/b}$ (生物碱 3, 4), $Me_9-H_7-H_8-Me_{10}$ (生物碱 5) 之间的偶合关系, 这些质子在大环中处于稳定的构象。其中, $H_{7/a}$ 由于接近吡啶环的平面, 受到较强的顺磁屏蔽效应, 移向低场, 例如生物碱 1、2, 该质子在 δ 3.981, 而 $H_{7/b}$ 离开这个平面, 出现在 δ 3.082附近, 这样, 导致二者化学位移的显著差别。生物碱 1 或 2 经 $NaOCH_3$ 酯交换得到的雷公藤酸二甲酯 (dimethyl wilfordate 6), 由于 H_2-7' 可以旋转, 所以这两个质子磁性几乎相同, 均出现在 δ 3.225 (2H, m) (图 7)。

2 位苯甲酰基或 β -呋喃酰基在这些生物碱中对有关质子是否有屏蔽效应, 为此, 均在 $CDCl_3$ 中测定生物碱 (1—5) 的倍半萜基醇母核上的质子化学位移以便比较 (表 2)。可以看出苯核或者呋喃核对生物碱 (1—4) 的 $H-6$, $H-7$, $H-8$, $H-9$, $Hb-11$ 几无影响, 但对 $H-1$, $H-2$, $H-3$, $Ha-11$ 以及 CH_3-12 均有不同程度的影响, 与化合物 5 的相应质子相比有明显的低场位移。这种低场位移现象, 显然来自苯核或呋喃核的屏蔽效应。2 位 $O-C$ 为竖键, 使苯核或者呋喃核伸向分子平面的上方, 推测, 它们的倾斜平面趋于 H_a-11 , $H-1$, $H-3$, $Me-12$ 所在的平面, 这些质子接近去屏蔽区, 导致低场位移, 而生物碱 (5) 的 2- β 乙酰基则不具备这样的屏蔽区, $H-2$ 的低场位移, 可能是诱导效应的结果, 而且苯核的屏蔽效应大于呋喃核。这可以说明 2- $C-O$ 键的 β 竖键取向。

表 1 昆明山海棠生物碱的UV, IR, MS光谱数据
Table 1. The UV, IR, MS spectral data of the alkaloids 1—5

alkaloids	UV λ_{MeCH} nm(ϵ) max	IR ν_{KBr} cm^{-1} max	MS [M^+] m/z
1. wilforine	228(13120)	3460, 1745	867
	267(3000)	1600, 1586, 1568, 1230, 715	
2. wilforgine	225(10880)	3435, 1740, 1625	857
	265(3780)	1580, 1560, 1225	
3. wilfortrine	224(10680)	3460, 1745, 1635	873
	265(4180)	1586, 1572	
4. wilfordine	222(18910)	3476, 1745, 1650	883
	266(3800)	1576, 1570, 710	
5. euonymine	223(8310)	3470, 1750, 1640	805
	267(3780)	1260, 1237	

表 2 生物碱 1—5 的 ^1H NMR 数据
Table 2. The ^1H NMR spectral data of the alkaloids 1—5. (500MHz, in CDCl_3 , TMS, δ , Hz)

alkaloids	wilforine (1)	wilforine (2)	wilforine (3)	wilfordine (4)	euonymine (5)
R^1	benzoyl	β -furanoyl	β -furanoyl	benzoyl	Ac
H —1	5.765(d, 3.5)	5.715(d, 3.5)	5.692(d, 3.5)	5.755(d, 3.5)	5.544(d, 4)
H —2	5.478(dd, 3.5, 2.5)	5.37(dd, 2.5, 3.5)	5.347(dd, 3.5, 2.5)	5.458(dd, 3.5, 3)	5.229(dd, 4, 2.5)
H —3	5.078(d, 2.5)	5.025(d, 2.5)	5.024(d, 2.5)	5.09(d, 3)	4.722(d, 2.5)
H —6	6.903(s)	6.85(s)	6.919(s)	6.94(s)	7.022(s)
H —7	2.37(d, 4)	2.352(d, 3.5)	2.366(d, 4)	2.388(d, 4)	2.337(d, 4)
H —8	5.552(dd, 6, 4)	5.55(dd, 6, 3.5)	5.532(dd, 6, 4)	5.535(dd, 6, 4)	5.504(dd, 6, 4)
H —9	5.407(d, 6)	5.402(d, 6)	5.394(d, 6)	5.392(d, 6)	5.348(d, 6)
H _a —11	5.515(d, 13)	5.514(d, 13)	5.552(d, 13.5)	5.56(d, 13)	5.126(d, 13.5)
H _b —11	4.399(d, 13)	4.296(d, 13)	4.308(d, 13.5)	4.408(d, 13)	4.48(d, 13.5)
H _a —15	5.752(d, 11.5)	5.757(d, 11.5)	5.83(d, 12)	5.804(d, 12)	5.846(d, 11)
H _b —15	3.79(d, 11.5)	3.785(d, 11.5)	3.742(d, 12)	3.755(d, 12)	3.692(d, 11)
M _e —12	1.673	1.584	1.618	1.718	1.543

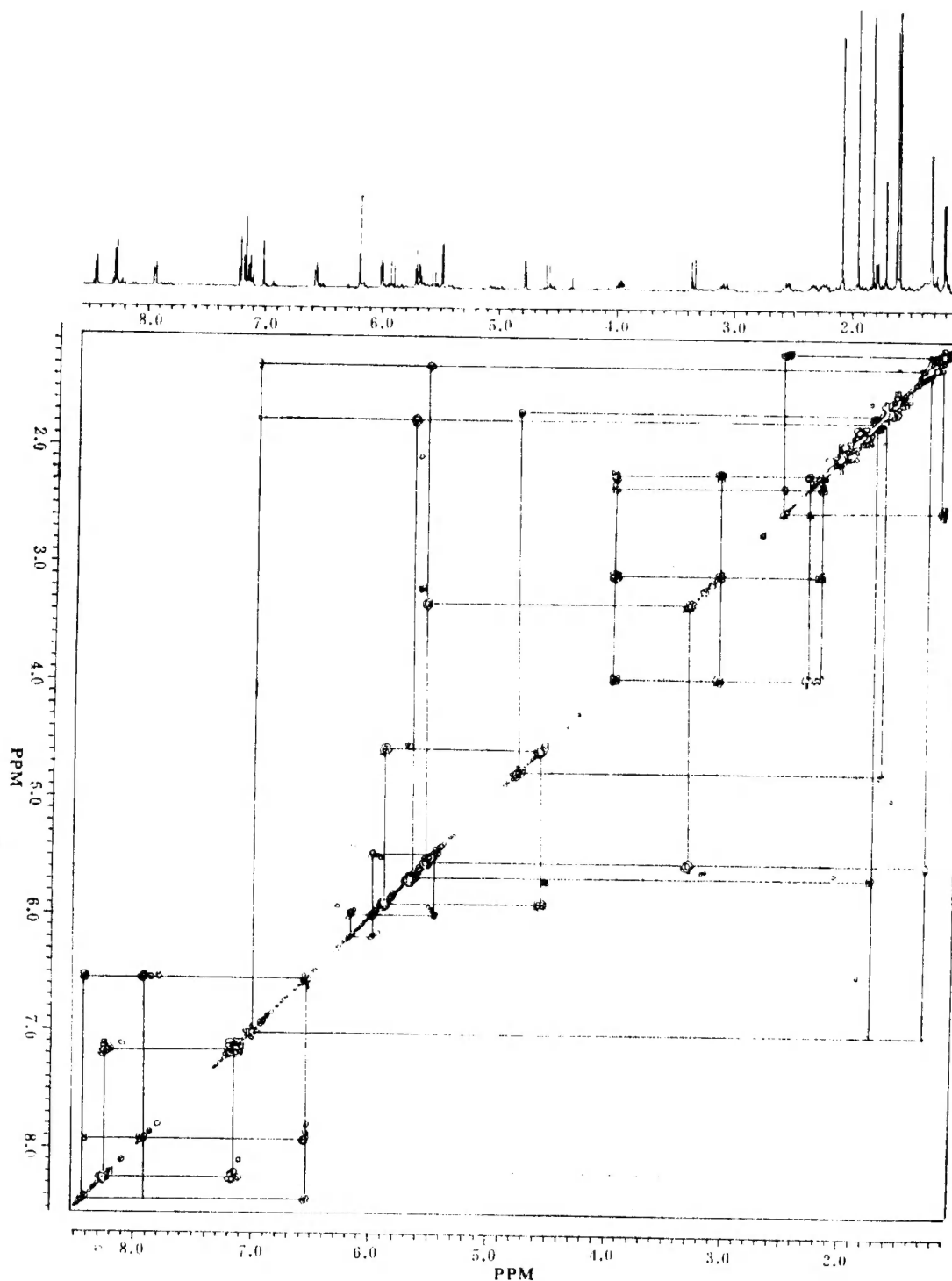


图3. 雷公藤次碱 (1) 的COSY谱 (500MHz, C_6D_6), 数据点阵 $S(F_1, F_2)$ 等高线图, 质子化学位移分别在频率 F_1, F_2 二维轴上。

Fig. 3. COSY (500MHz, C_6D_6) spectrum of wilforine (1) presented as a contour plot of the $S(F_1, F_2)$ data matrix (δ^1H in two dimensions),

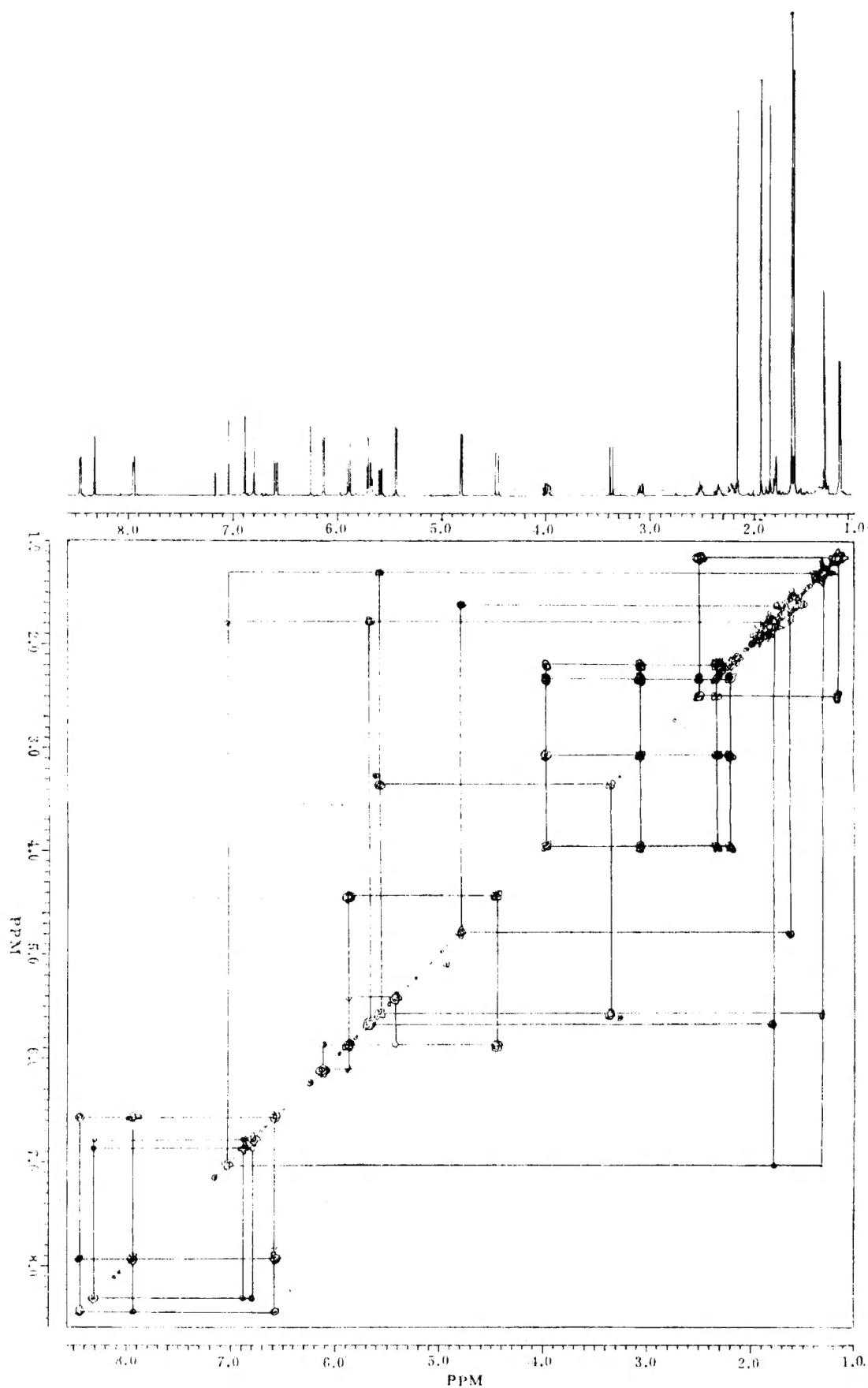


图4. 雷公藤碱乙(2)的COSY谱(500MHz, C₆D₆), 数据点阵S(F₁, F₂)等高线图, 质子化学位移分别在频率F₁, F₂二维轴上。

Fig. 4. COSY(500MHz, C₆D₆) spectrum of wilforgine(2) presented as a contour plot of the S(F₁, F₂) data matrix (δ ¹H in two dimensions)

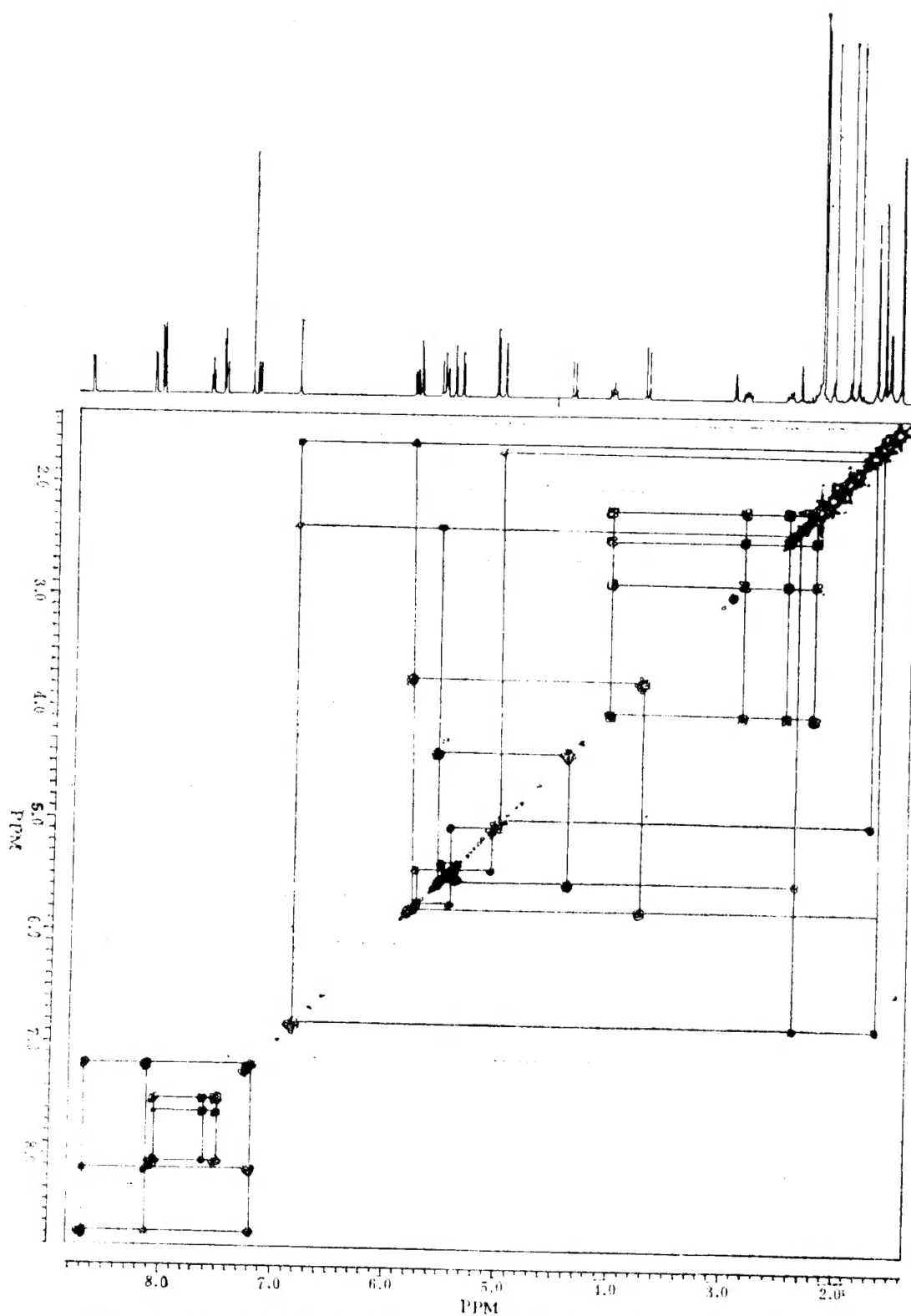


图5. 雷公藤碱(4)的COSY谱(500MHz, CDCl_3), 数据点阵 $S(F_1, F_2)$ 等高线图, 质子化学位移分别在频率 F_1, F_2 二维轴上

Fig. 5. COSY(500MHz, CDCl_3) spectrum of wilfordine(4) presented as a contour plot of the $S(F_1, F_2)$ data matrix ($\delta^1\text{H}$ in two dimensions).

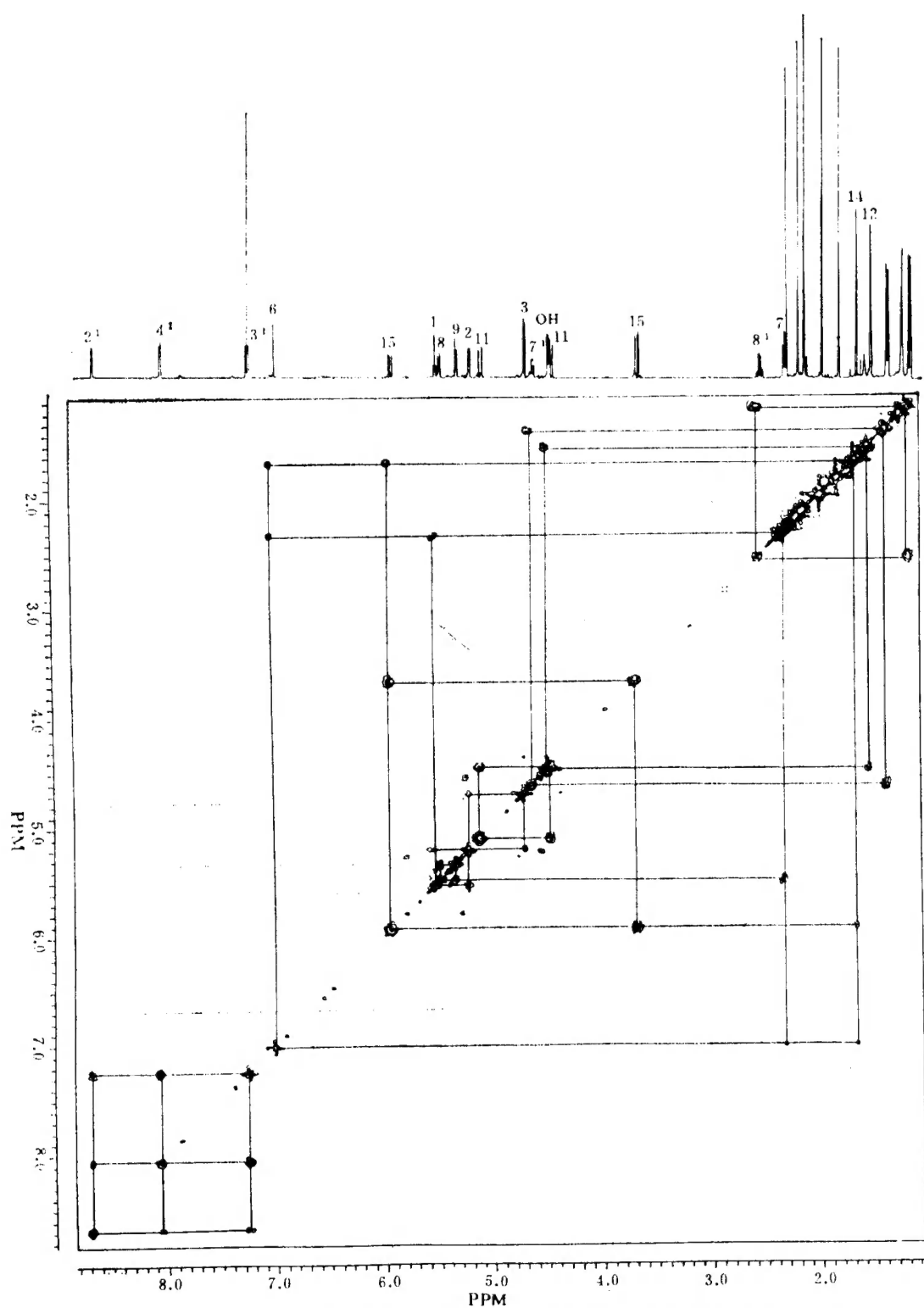


图6. 卫矛碱 (5) 的COSY谱 (500MHz, CDCl_3), 数据点阵 $S(F_1, F_2)$ 等高线图, 质子化学位移分别在频率 F_1, F_2 二维轴上。

Fig. 6. COSY (500MHz, CDCl_3) spectrum of euonymine (5) presented as a contour plot of $S(F_1, F_2)$ data matrix ($\delta^1\text{H}$ in two dimensions).

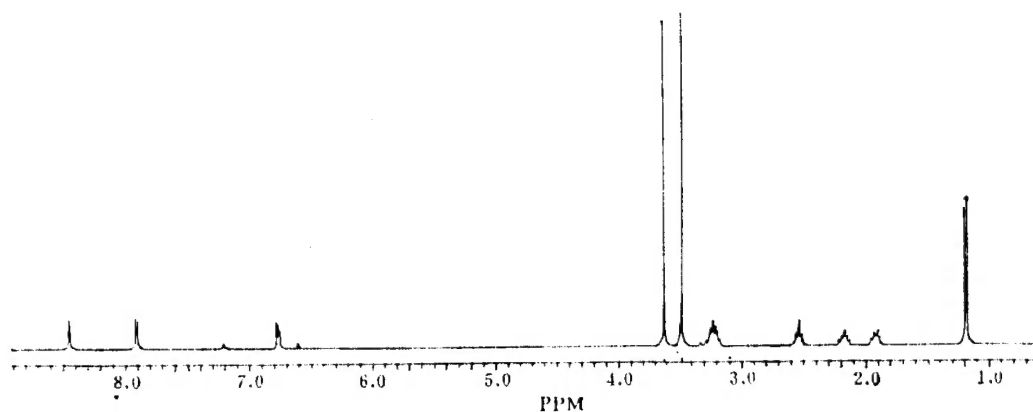
图7. 雷公藤酸二甲酯的 ^1H NMR谱

Fig. 7. The ^1H NMR spectrum of dimethyl wilfordate (500MHz, $\text{C}_6\text{D}_6 + \text{CDCl}_3$ 1:1, TMS, δ)

实 验 部 分

Prof. Dr. E. Hecker (Institut für Biochemie, Deutsches Krebsforschungszentrum, Heidelberg, F. R. G.) 提供分离和鉴定昆明山海棠生物碱的实验条件。Dr. H. J. Opferkuch测定核磁共振光谱及“COSY”谱, 均用Bruker AM-500核磁共振光谱仪, 溶剂分别为: C_6D_6 , CDCl_3 , TMS作内标, 化学位移 δ 值, 偶合常数单位 Hz 。质谱用Finnigan-MAT (Bremen) MAT-711测定。红外光谱用Perkin-Elmer 580B测定, KBr压片。紫外光谱用Beckmann Acta MV1测定, MeOH作溶剂。

生物碱的提取和分离 昆明山海棠根粉用甲醇回流三次, 回收甲醇, 加水, 醋酸乙酯抽提五次。蒸干醋酸乙酯, 复用氯仿溶解, 溶解物转入醋酸乙酯中, 过氧化铝柱, 醋酸乙酯洗脱, 收集含生物碱的馏分, 用甲醇结晶。此混合结晶采用烷化硅胶RP-18薄层层析 ($\text{MeOH}-\text{H}_2\text{O}$ 8:2) 并纯化, 即得生物碱 (1—5)。

雷公藤碱乙 (2): MS (m/z): 857 (M^+). UV $\lambda_{\text{max}}^{\text{MeOH}}$ nm (ϵ): 225 (10880), 265 (3780). IR $\nu_{\text{max}}^{\text{KBr}}$ cm^{-1} : 3435, 1740, 1625, 1580, 1560, 1225. ^1H NMR (in C_6D_6): 8.448 (1H, dd, $J_{2,1}, 4,1=2\text{Hz}$, $J_{2,1}, 3,1=5\text{Hz}$, H-2'), 8.315 (1H, q, $J_{2,1}, 4,1=J_{2,1}, 5,1=1\text{Hz}$, H-2''), 7.94 (1H, dd, $J_{2,1}, 4,1=2\text{Hz}$, $J_{4,1}, 3,1=8\text{Hz}$, H-4'), 7.037 (1H, bs, H-6), 6.878 (1H, q, $J_{2,1}, 4,1=1\text{Hz}$, $J_{4,1}, 5,1=2\text{Hz}$, H-4''), 6.79 (1H, dd, $J_{2,1}, 5,1=1\text{Hz}$, $J_{4,1}, 5,1=2\text{Hz}$, H-5''), 6.858 (1H, dd, $J_{2,1}, 3,1=5\text{Hz}$, $J_{3,1}, 4,1=8\text{Hz}$, H-3'), 6.126 (1H, d, $J_{1,2}=4\text{Hz}$, H-1), 5.887 (1H, $J_{11a, 11b}=14.5\text{Hz}$, H_a-11), 5.875 (1H, dd, $J_{1,2}=4\text{Hz}$, $J_{2,3}=2.5\text{Hz}$, H-2), 5.688 (1H, d, $J_{8,9}=6\text{Hz}$, H-9), 5.667 (1H, dd, $J_{8,9}=6\text{Hz}$, $J_{7,8}=4\text{Hz}$, H-8), 5.576 (1H, d, $J_{15a, 15b}=12\text{Hz}$, H_a-15), 5.427 (1H, d, $J_{2,3}=2.5\text{Hz}$, H-3), 4.802 (1H, dd, $J=1\text{Hz}$, D_2O 交换消失, OH-4), 4.456 (1H, d, $J_{11a, 11b}=14.5$, H_b-11), 3.981 (1H, ddd, $J_{7/a, 7/b}=14\text{Hz}$, $J_{7/a, 8/a}=7\text{Hz}$, $J_{7/a, 8/b}=9\text{Hz}$, H_a-7'), 3.362 (1H, d, $J_{15a, 15b}=12\text{Hz}$, H_b-15), 3.082 (1H, ddd, $J_{7/a, b}=14\text{Hz}$, $J_{7/b, 8/a}=5\text{Hz}$, $J_{7/b, 8/b}=$

7H_Z, H_b—7'), 2.515 (1H, qdd, J_{9/}, 10/ = 7H_Z, J_{9/}, 8/a = 10H_Z, J_{9/}, 8/b = 2.5H_Z, H—9'), 2.342 (1H, dddd, J_{8/a}, b = 14H_Z, J_{8/a}, 9/ = 10H_Z, J_{8/a}, 7/a = 7H_Z, J_{8/a}, 7/b = 5H_Z, H_a—8'), 2.21 (1H, dddd, J_{8/a}, b = 14H_Z, J_{8/a}, 9/ = 2.5H_Z, J_{8/b}, 7/a = 9H_Z, J_{8/b}, 7/b = 7H_Z, H_b—8'), 1.792 (1H, d, J₆, 7 = 4H_Z, H—7), 2.154, 1.933, 1.823, 1.623, 1.608 (each 3H, Ac × 5), 1.625 (3H, d, J = 1H_Z, CH₃—12), 1.323 (3H, s, CH₃—14), 1.175 (3H, d, J_{9/}, 10/ = 7H_Z, CH₃—10').

雷公藤碱丁 (3): MS(m/z): 873(M⁺). UV λ_{max}^{MeOH} nm(ε): 224(10690), 265(4180). IR ν_{max}^{KBr} cm⁻¹: 3460, 1745, 1586, 1572. ¹H NMR(in CDCl₃): 8.692 (1H, dd, J_{2/}, 4/ = 1.5H_Z, J_{2/}, 3/ = 5H_Z, H—2'), 8.254 (1H, bs, H—2''), 8.13(1H, dd, J_{2/}, 4/ = 1.5H_Z, J_{3/}, 4/ = 8H_Z, H—4'), 7.492(1H, dd, J_{2/}, 5/ = 1.5H_Z, J_{2/}, 4/ = 2H_Z, H—2''), 7.205(1H, dd, J_{2/}, 3/ = 5H_Z, J_{3/}, 4/ = 8H_Z, H—3'), 6.919(1H, s, H—6), 6.833(1H, dd, J_{2/}, 5/ = 2H_Z, H—5''), 5.83 (1H, d, J_{15a}, b = 12H_Z, H_a—15), 5.692(1H, d, J₁, 2 = 3.5H_Z, H—1), 5.552 (1H, d, J_{11a}, b = 13.5H_Z, H_a—11), 5.532(1H, dd, J₇, 8 = 4H_Z, J₈, 9 = 6H_Z, H—8), 5.394(1H, d, J₈, 9 = 6H_Z, H—9), 5.347(1H, dd, J₁, 2 = 3.5H_Z, J₂, 3 = 3H_Z, H—2), 5.052(1H, d, J = 1H_Z, D₂O交换消失, OH—4), 5.024 (1H, d, J₂, 3 = 3H_Z, H—3), 4.308(1H, d, J_{11a}, b = 13.5H_Z, H_b—11), 4.054 (1H, ddd, J_{7/a}, b = 14H_Z, J_{7/a}, 8/a = 9H_Z, J_{7/a}, 8/b = 5H_Z, H_a—7'), 3.724(1H, d, J_{15a}, b = 12H_Z, H_b—15), 2.866(1H, ddd, J_{7/a}, b = 14H_Z, J_{7/b}, 8/a = 7H_Z, J_{7/b}, 8/b = 5H_Z, H_b—7'), 2.496(1H, ddd, J_{8/a}, b = 14H_Z, J_{8/a}, 7/b = 7H_Z, J_{8/a}, 7/a = 5H_Z, H_a—8'), 2.366(1H, d, J₆, 7 = 4H_Z, H—7), 2.23(1H, ddd, J_{8/a}, b = 14H_Z, J_{8/b}, 7/a = 7H_Z, J_{8/b}, 7/b = 5H_Z, H_b—8'), 2.25, 2.21, 2.20, 1.976, 1.867(each 3H, s, Ac × 5), 1.642(3H, s, CH₃—14), 1.618(3H, J = 1H_Z, CH₃—12), 1.477(3H, s, CH₃—10').

雷公藤碱 (4): MS(m/z): 883(M⁺). UV λ_{max}^{MeOH} nm(ε): 225(18910), 266(3800). IR ν_{max}^{KBr} cm⁻¹: 3476, 1745, 1650, 1576, 1570, 710. ¹H NMR(in CDCl₃): 8.672(1H, dd, J_{2/}, 4/ = 1.5H_Z, J_{2/}, 3/ = 5H_Z, H—2'), 8.134(1H, dd, J_{2/}, 4/ = 1.5H_Z, J_{3/}, 4/ = 8H_Z, H—4'), 8.065(2H, dd, J = 1.5H_Z, J = 8H_Z, H—2'', 6''), 7.625(1H, tt, J = 1H_Z, J = 8H_Z, H—4''), 7.507(2H, dt, J = 1H_Z, J = 8H_Z, H—3'', 5''), 7.204(1H, dd, J_{2/}, 3/ = 5H_Z, J_{3/}, 4/ = 8H_Z, H—3'), 6.94(1H, s, H—6), 5.804(1H, d, J_{15a}, b = 12H_Z, H_a—15), 5.755(1H, d, J₁, 2 = 3.5H_Z, H—1), 5.56(1H, d, J_{11a}, b = 13H_Z, H_a—11), 5.535(1H, dd, J₇, 8 = 4H_Z, J₈, 9 = 6H_Z, H—8), 5.458(1H, dd, J₁, 2 = 3.5H_Z, J₂, 3 = 3H_Z, H—2), 5.392(1H, J₈, 9 = 6H_Z, H—9), 5.09(1H, d, J₂, 3 = 3H_Z, H—3), 5.012(1H, d, J = 1H_Z, OH—4), 4.408(1H, d, J_{11a}, b = 13H_Z, H_b—11), 4.053 (1H, ddd, J_{7/a}, b = 14H_Z, J_{7/a}, 8/b = 9H_Z, J_{7/a}, 8/a = 5H_Z, H_a—7'), 3.755 (1H, d, J_{15a}, b = 12H_Z, H_b—15), 2.87(1H, ddd, J_{7/a}, b = 14H_Z, J_{7/b}, 8/a =

$7H_Z$, $J_{7/b, 8/b}=5H_Z$, H_b-7'), 2.482(1H, ddd, $J_{8/a, b}=14H_Z$, $J_{8/a, 7/b}=7H_Z$, $J_{8/a, 7/a}=5H_Z$, H_a-8'), 2.388(1H, d, $J_{6, 7}=4H_Z$, $H-7$), 2.226(1H, ddd, $J_{8/a, b}=14H_Z$, $J_{8/b, 7/a}=9H_Z$, $J_{8/b, 7/a}=5H_Z$, H_b-8'), 2.202, 2.188, 2.094, 1.941, 1.872(each 3H, Ac \times 5), 1.718(3H, d, $J=1H_Z$, CH_3-12), 1.648(3H, s, CH_3-14), 1.503(1H, s, CH_3-10').

卫矛碱 (5): MS(m/z): 805(M^+). UV λ_{max}^{MeOH} nm(ϵ): 223(8310), 267(3780). IR ν_{max}^{KBr} cm^{-1} : 3470, 1750, 1260, 1237, 1640. 1H NMR(in $CDCl_3$): 8.688(1H, dd, $J_{2/, 4/}=1.5H_Z$, $J_{2/, 3/}=5H_Z$, $H-2'$), 8.026(1H, dd, $J_{2/, 4/}=1.5H_Z$, $J_{3/, 4/}=8H_Z$, $H-4'$), 7.258(1H, dd, $J_{2/, 3/}=5H_Z$, $J_{3/, 4/}=8H_Z$, $H-3'$), 7.022(1H, s, $H-6$), 5.846(1H, d, $J_{15a, b}=12H_Z$, H_a-15), 5.544(1H, d, $J_{1, 2}=4H_Z$, $H-1$), 5.504(1H, dd, $J_{7, 8}=4H_Z$, $J_{8, 9}=6H_Z$, $H-8$), 5.348(1H, d, $J_{8, 9}=6H_Z$, $H-9$), 5.229(1H, dd, $J_{1, 2}=4H_Z$, $J_{2, 3}=2.5H_Z$, $H-2$), 5.126(1H, d, $J_{11a, b}=13.5H_Z$, H_a-11), 4.722(1H, d, $J_{2, 3}=2.5H_Z$, $H-3$), 4.647(1H, qd, $J_{7/, 9/}=7H_Z$, $J_{7/, 8/}=1H_Z$, $H-7'$), 4.503(1H, d, $J=1H_Z$, D_2O 交换消失, $OH-4$), 4.48(1H, d, $J_{11a, b}=13.5H_Z$, H_b-11), 3.692(1H, d, $J_{15a, b}=12H_Z$, H_b-15), 2.563(1H, qd, $J_{8/, 9/}=7H_Z$, $J_{8/, 7/}=1H_Z$, $H-8'$), 2.337(1H, d, $J_{7, 8}=4H_Z$, $H-7$), 2.32, 2.21, 2.156, 2.151, 1.982, 1.835(each 3H, s, Ac \times 6), 1.675(3H, s, CH_3-14), 1.543(3H, d, $J=1H_Z$, CH_3-12), 1.389(3H, d, $J_{7/, 9/}=7H_Z$, CH_3-9'), 1.188(3H, d, $J_{8/, 10/}=7H_Z$, CH_3-10').

雷公藤乙(2)的酯交换 20mg雷公藤碱乙溶于0.1M的甲醇钠 甲醇溶液10ml中, 放置过夜, 倾入磷酸缓冲液(pH 7), 乙醚提取, 水洗, 无水硫酸钠干燥, 除去溶剂得油状物, 制备性硅胶薄层层析纯化, 得油状物雷公藤酸二甲酯(6), 5 mg. MS: m/z 251(M^+) UV λ_{max}^{MeOH} nm(ϵ): 218(8030), 265(3240). IR ν_{max}^{KBr} cm^{-1} : 1723, 1580, 1565, 1256, 1275. 1H NMR(in $C_6D_6 + CDCl_3$ 1:1): 8.448(1H, $J_{2/, 4/}=1.5H_Z$, $J_{2/, 3/}=5H_Z$, $H-2'$), 7.907(1H, $J_{2/, 4/}=1.5H_Z$, $J_{3/, 4/}=8H_Z$, $H-4'$), 6.765(1H, $J_{2/, 3/}=5H_Z$, $J_{3/, 4/}=8H_Z$, $H-3'$), 3.47, 3.63(each 3H, s, OCH_3), 3.225(2H, m, H_2-717), 2.536(1H, six. $J=7H_Z$, $H-9'$), 2.173, 1.918(each 1H, m, H_2-8'), 1.183(3H, d, $J=7H_Z$, CH_3-10').

致谢: W. Rubik和E. Krambs先生(Institut für Biochemie, Deutsches Krebsforschungszentrum, Heidelberg, F. R. G.) 帮助测定MS, IR, UV光谱。

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APPLICATION OF THE "COSY" SPECTRA TO THE IDENTIFICATION AND COMPLETE ASSIGNMENT OF ^1H OF THE ALKALOIDS FROM *TRIPTERYGIUM HYPOGLAUCUM*

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Abstract The alkaloids from *Tripterygium hypoglaucum* (Lévl) Hutch. and their structure are unknown, except wilforine reported by the author in the last paper [1]. This continuing investigation reports the structural identification of wilforgine (2), wilfordine (4), wilfortrine (3) and euonymine (5) from this plant by the chemical and spectroscopic methods. The "COSY" ^1H — ^1H chemicalshift correlation provides the ^1H scalar coupling relationships for the purpose of the complete assignment of ^1H , and the relative configuration of them. In addition, the structure of wilforgine and wilfortrine was not elucidated by ^1H NMR spectra, although both have early been isolated from species *Tripterygium wilfordii* Hook. f.

Key words *Tripterygium hypoglaucum*, Wilforine, Wilforgine, Wilfortrine, Wilfordine, Euonymine, "COSY" spectra